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Effect of ZnO Double Layer as Anti-Reflection Coating Layer in ZnO Dye-Sensitized Solar Cells.

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Abstract

Dye-sensitized solar cells based on ZnO double layer anti-reflection coating (DLARC) thin films are investigated. The ZnO DLARCs were prepared by stacking two different ZnO morphologies prepared by two different techniques including rf-magneton sputtering (rf-ZnO) and sparking technique (sp-ZnO). The device using rf-ZnO as the bottom layer and sp-ZnO (3 cycles) as the top one exhibits short circuit current density (J_{sc}) of 5.80 mA/cm^2 and the maximum power conversion efficiency (*PCE*) of 1.88 %, which is higher than that of the device stacking in reverse order and the device using ZnO single layer anti-reflection coating (SLARC). The main enhancement of *PCE* is attributed to the reduction of light reflection at the substrate surface. This leads to the increase of J_{sc} and the efficiency improvement of DSSCs.

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Keywords: ZnO; dye-sensitized solar cells; Double anti-reflection coating layer; Sputtering process; Sparking technique.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been widely paid attention due to their great potential for low cost energy conversion devices. However, DSSCs show low power conversion efficiency (*PCE*) because of some efficiency losses, such as reflection of light by a substrate, charge recombination and carrier trapping in a material and surface, power dispersion due to the resistance of cell (material, metal, electrode, etc)

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Approaches to improve the power conversion efficiency of DSSCs are to reduce these losses. Reduction of light reflection by using double layer anti-reflection coatings (DLARCs) is one of the effective approaches [1]. DLARCs are expected to reduce the reflection and increase the transmission of light at the glass surface. These lead to an increase of the total flux of photons to photocurrent through the electrode and short circuit current density (J_{sc}), as shown in equation (1) [2].

$$J_{sc} = \int_{\lambda_1}^{\lambda_2} qF(\lambda)[1 - R(\lambda) + S(\lambda)]Q_i(\lambda)d\lambda \quad (1)$$

where q is elementary charge, λ_1 and λ_2 are the wavelength limits, $F(\lambda)$ is spectral solar flux (flux of the solar spectrum), $R(\lambda)$ is reflection of light, $S(\lambda)$ is scattering factor and $Q_i(\lambda)$ is internal quantum efficiency. Consequently, the power conversion efficiency (PCE) of the variation of solar energy can be calculated from the following equation (2) [2]

$$PCE = \frac{J_{SC} V_{OC} FF}{P_{in}} \quad (2)$$

where the fill factor (FF) is a measure of the quality of the a solar cell, P_{in} is the sum of the radiation incident on the solar cell, J_{sc} is the short circuit current density, and V_{oc} is the open circuit voltage.

According to equation (1) and (2), the decrease in reflectance $R(\lambda)$ leads to the increase in J_{sc} and power conversion efficiency of DSSC devices. The anti-reflection coating layers (ARCLs) are usually applied on the surface of material to reduce light reflection and increase light transmission. In solar cell technology, many DLARC coating processes have been used in various devices, such as on the surface of silicon, $CuInGaSe_2$ (CIGS), organic solar cell and DSSCs. Coating examples are SiN_x/SiO_2 on Si solar cells [3], SiO_x/ITO on Si solar cells [4], ZnO/TiO_2 coating on Si solar cells [5] and ZnO sputtering thin flim on DSSCs [2].

Among these materials, nanostructured ZnO thin films have great potential for ARCLs in DSSCs because of with their high transparency in the visible region and ability to form textured coating via anisotropic growth [5]. Moreover, ZnO nanostructures are the moth eye structure as natural nanostructures films which eliminate reflections [6]. Thickness, surface roughness, diameter and shape of ZnO nanostructures play a role in determination of the values of refractive index and the light reflection. Therefore, nanostructured ZnO thin films as ARCLs show a high possibility to improve the power conversion efficiency of DSSCs.

In this work, two different morphologies of ZnO thin films are prepared by two different techniques including rf-magneton sputtering process and sparking technique. Two of them are stacked onto each other and used as DLARCs in DSSCs. Optical properties and photovoltaic characteristics have been also investigated.

2. Experimental

DLARCs were prepared by stacking two different ZnO morphologies prepared by two different techniques including rf-magneton sputtering (rf-ZnO) and sparking technique (sp-ZnO). Rf-magneton sputtering (rf-ZnO) was performed for 60 minute under an atmosphere of Ar at 2.5×10^{-2} torr and sputtering power of 150 watts. Sparking technique was carried out by applying high voltage when the 25 nF capacitor was changed to 10 kV for two Zn wires sharp and connected it by rotating control switch with 1 (sp1-ZnO), 3 (sp3-ZnO), 5 (sp5-ZnO) sparking cycles. The rf-ZnO and sp-ZnO were deposited onto a FTO substrate in different order. The former sample was prepared by using sp-ZnO as the bottom layer and rf-ZnO as the top one, denoted as sp-ZnO/rf-ZnO. The latter one was prepared in reverse order, denoted as rf-ZnO/sp-ZnO as shown in Figure 1. (b)-(c). The samples were annealed at 450ºC for 1 hr in the air before the fabrication of DSSCs. Surface and cross-sectional morphologies were characterized by field emission scanning electron microscopy (FE-SEM). Also, optical properties were studied by measurement of transmittance and reflectance via UV-vis spectroscopy. In addition, refractive index was obtained via ellipsometry. The fabrication of DSSCs was patterned after the previous reports [2, 7-10]. The DSSCs were composed of ZnO DLARCs /glass/ fluorine-doped tin oxide (FTO)/ZnO as a photoelectrode, dye sensitizer, iodine/iodide solution as an electrolyte and Pt / fluorine-doped tin oxide (FTO)/glass as a counterelectrode, as shown in Figure 1. (a). N719 dye (Solaronix, Switzerland) as photo-sensitizer was dissolved in acetonitrile (CH_3CN purity) and tert-butanol ($(CH_3)_3COH$, anhydrous, ≥99.5%) (1:1) with a concentration of 0.5 mM. Finally, photovoltaic characteristics of the DSSCs were tested under stimulated sunlight AM 1.5 with a radiant power of 100 mW/cm^2.

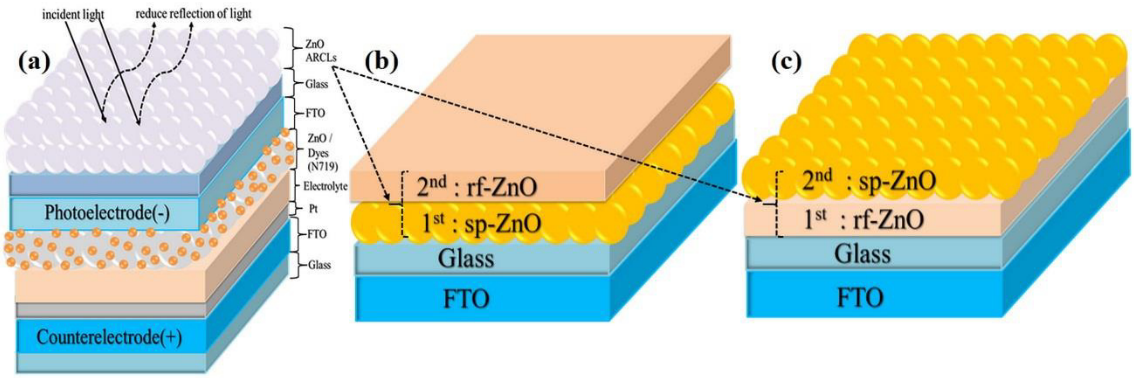

Fig. 1. Schematic diagram of (a) DSSCs structure with ZnO double layer anti-reflection coating (DLARC) thin films prepared by stacking two different ZnO morphologies, (b) with rf-ZnO/sp-ZnO/glass/FTO and (c) sp-ZnO/rf-ZnO/glass/FTO.

3. Results and Discussions

Morphology of nanostructured ZnO thin films coated on a glass substrate have been observed. Figure 2. (a)-(c) shows FE-SEM images of sp(1,3,5)-ZnO/rf-ZnO. It is seen that the grain size of sp(1,3,5)-ZnO/rf-ZnO (100-500 nm) is bigger than that of rf-ZnO/sp(1,3,5)-ZnO (Figure 2. (d)-(f)) with diameter of about 20 nm. The different grain size of sp(1,3,5)-ZnO prepared by the same technique is because of different in morphology of the bottom seed layer. Generally, particle size of nanostructures, thickness and refractive index are the parameters for determining the light scattering, absorption and transmission.

Figure 3. , the thickness of ZnO DLARCs with the condition sp(1,3,5)-ZnO/rf-ZnO are thinner than that of rf-ZnO/sp(1,3,5)-ZnO. It is seen that samples prepared in different order have different film thickness. This is probably because some sp-ZnO nanoparticles are scattered during the sputtering process of rf-ZnO. Therefore, the sparking cycle was added to increase the thickness of ZnO DLARCs and density of ZnO nanoparticles.

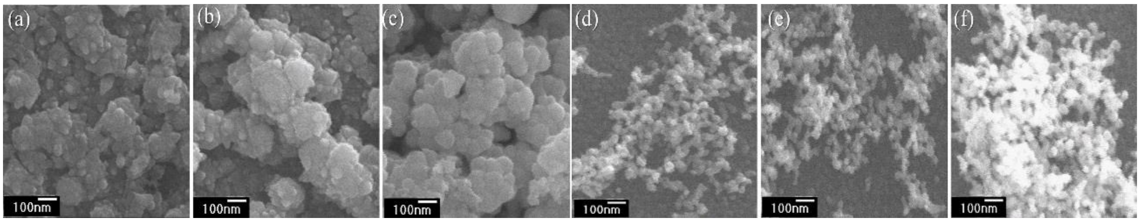

Fig. 2. Top-view FE-SEM images of ZnO DLARCs; (a) sp1-ZnO/rf-ZnO, (b) sp3-ZnO/rf-ZnO, (c) sp5-ZnO/rf-ZnO, (d) rf-ZnO/sp1-ZnO, (e) rf-ZnO/sp3-ZnO and (f) rf-ZnO/sp5-ZnO films.

Optical properties related to the surface morphology have been investigated and can be explained by Rayliegh light scattering [11, 12]. In Figure 4. (a), transmittance spectra of rf-ZnO/sp(1,3,5)-ZnO DLARCs are higher than that of sp(1,3,5)-ZnO/rf-ZnO, the ZnO single layer anti-reflection coating (rf-ZnO) and the reference (glass). This is because when the size of nanostructures becomes equivalent to or greater than the wavelength of incident light, high multiple light scattering and low transmission occurs. On the other hand, the opposite effects happen when the size is smaller. [11, 12]. Therefore, the results of FE-SEM image in Figure 2. (d)-(f) have the size smaller than that Figure 2. (a)-(c) and the wavelenght of light. Also, the light can be high transmission and high forward light scattering on ZnO DLARCs with rf-ZnO/sp(1,3,5)-ZnO. Especially, the rf-ZnO/sp3-ZnO shows the highest transmittance of 89.17% among the films prepared by other conditions.

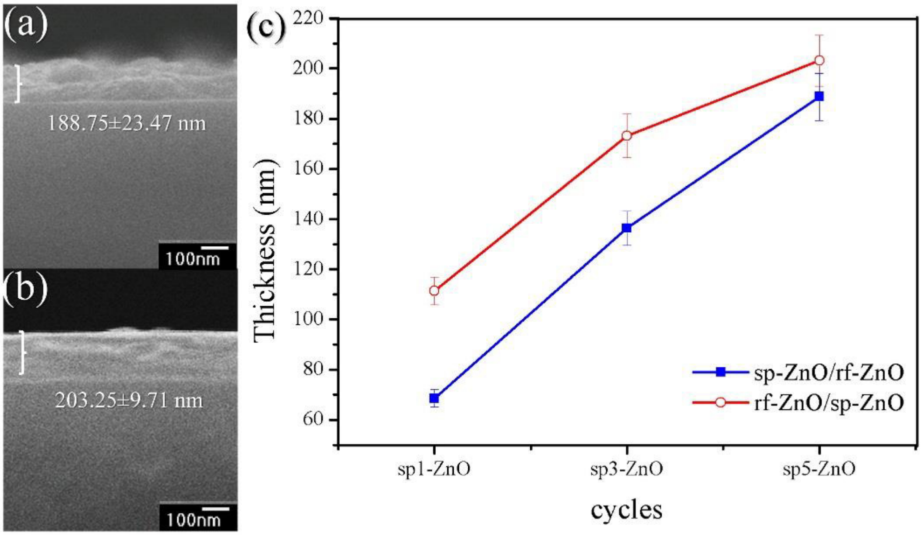

Fig. 3. Cross-sectional FE-SEM images of ZnO DLARCs; (a) sp5-ZnO/rf-ZnO, (b) rf-ZnO/sp5-ZnO films and (c) films thickness as a function of sparking cycles.

Reflectance of the samples are show in Figure 4. (b). It is seen that reflectance of all ZnO DLARCs are lower than that of the rf-ZnO and glass. This indicates that of ZnO DLARCs are appropriate for the anti-reflection of light on the surface. Particularly, the sp(1,3,5)-ZnO/rf-ZnO samples increase light transmition and reduce the reflection of light. Moreover, the higher transmittance of rf-ZnO/sp(1,3,5)-ZnO DLARCs is due to the lower refractive index of the rf-ZnO/sp(1,3,5)-ZnO as shown in Figure 5. (a). Therefore, light travels through the rf-ZnO/sp(1,3,5)-ZnO films faster than the other conditions.

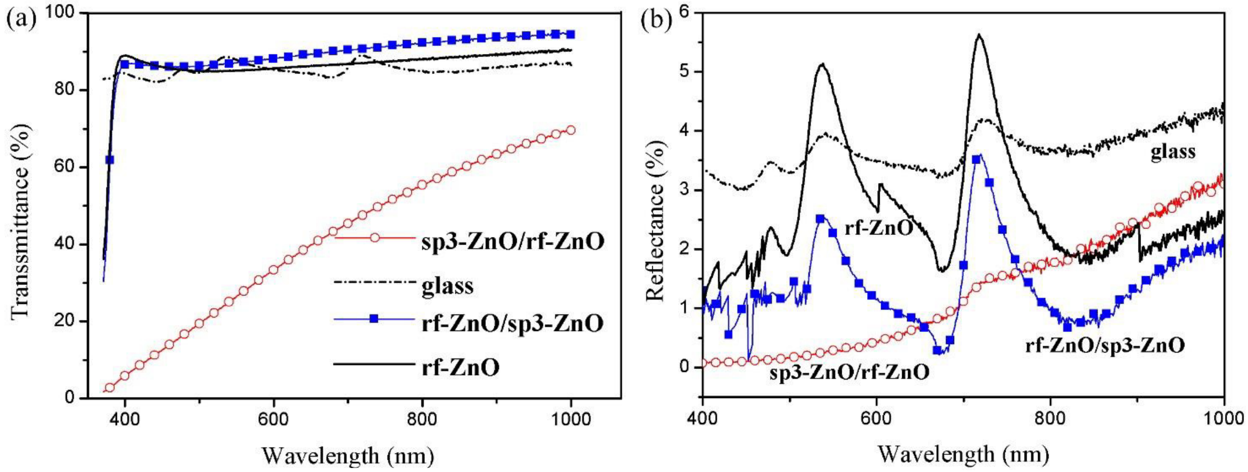

Fig. 4. (a) the optical transmittance spectra and (b) the optical reflectance spectra of ZnO DLARCs.

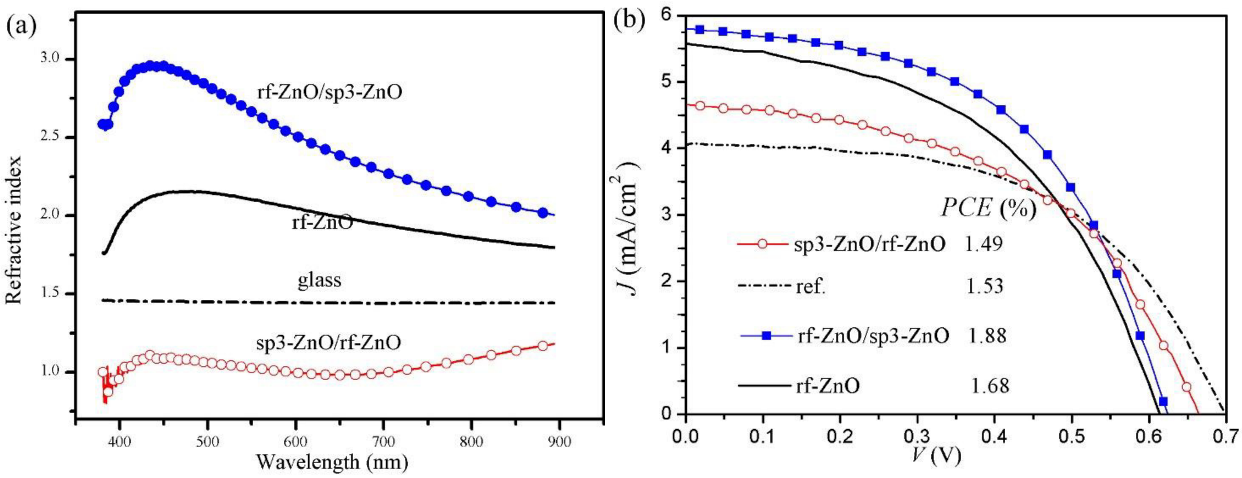

Fig. 5. (a) optical refractive index spectra of ZnO DLARCs and (d) photovoltaic performance of the DSSCs fabricated with ZnO DLARCs.

Table 1. The optical properties and electrical properties of the DSSCs fabricated with ZnO DLARCs.

Sample	J_{sc}(mA/cm^2)	Reflectance (%)	Transmittance (%)	*PCE*(%)	*FF* (%)
ref	4.07	3.37	85.41	1.53	54
rf-ZnO	5.58	2.43	86.61	1.68	49
rf-ZnO/sp1-ZnO	5.51	1.74	84.98	1.74	55
rf-ZnO/sp3-ZnO	5.80	1.23	89.17	1.88	52
rf-ZnO/sp5-ZnO	5.51	1.84	82.62	1.53	50
sp1-ZnO/rf-ZnO	4.76	1.43	81.21	1.53	47
sp3-ZnO/rf-ZnO	4.66	0.53	40.75	1.49	44
sp5-ZnO/rf-ZnO	3.63	0.32	43.57	1.28	52

Figure 5. (b) and Table 1. show photovoltaic performances and optical properties of the DSSCs of the DSSCs fabricated with ZnO DLARCs. The rf-ZnO/sp3-ZnO device exhibites J_{sc} of 5.80 mA/cm^2 and the maximum *PCE* of 1.88 %, which is higher than that of the reference cell (4.07 mA/cm^2, 1.53%). The rf-ZnO/sp3-ZnO has the highest *PCE* because it has the highest transmittance, reduced reflectance and increaesed $S(\lambda)$. This leads to the increase in J_{sc} and *PCE* as described by equation (1) and (2).

4. Conclusion

ZnO DLARCs prepared by rf- sputtering technique for the first layer and sparking process for second layer can be successfully used for efficiency enhancement of DSSCs. The optimal condition is rf-ZnO/sp3-ZnO with short circuit current density (J_{sc}) of 5.80 mA/cm^2 and the maximum power conversion efficiency (*PCE*) of 1.88 %, which is higher than that of the device stacking in reverse order and the device using ZnO single layer anti-reflection coating (rf-ZnO). The main enhancement of *PCE* is attributed to reduction of light reflection and increase the transmission of light at the substrate surface resulting in anincrease of J_{sc} and higher *PCE*.

Acknowledgment

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